Technical Memo

Shaw Environmental and Infrastructure, Inc.
Contract No. EP-C-08-034

In reply refer to: 12-JSC-04

Date: May 30, 2012

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Subject: 8OA878DW

Task: 24274

Project: Geochemical Impacts

INTRODUCTION

Technical Memo 12-JSC-03 (TD8OA865CS) details the methodology used for the analysis of the 7 samples submitted under 8OA878DW. The results are to be considered as estimates as the C1-C4 Alcohol method is still in development and not all DQO's have been established.

METHOD AND MATERIALS

Column:
Restek RTX-624, 60 meter length, 0.53 mm ID with 3µ film thickness, catalog number 241580

OI Eclipse Purge-and-Trap with Infra-sparge heater:
Kit 4660 Sample heater 115v Item number 321732

Trap:

#7 Tenax only P&T Item number 227348

Standards:

Supelco C1-C4 Alcohols in water catalog number 21495418 Lot number LB90709 (methanol, ethanol, 2-propanol, tertiary butyl alcohol, n-propanol, 2-butanol, isobutanol, 1-butanol)
Restek C1-C4 Alcohols in water catalog number 566852 Lot number A086968

Working standards preparation:

C1-C4 Alcohols in water
Supelco Lot# LB90709

units are ppb in 100 mls water
Stock A-10000 ppm in water (ampoule)
Stock B-100 ul of stock A in 900 uls water

ppm			ppb
Stock	amt of stock	amt water	Std Conc
1000 (B)	5 ul	100	50
1000 (B)	10 ul	100	100
1000 (B)	25 ul	100	250
10000(A)	5 ul	100	500
10000(A)	10 ul	100	1000

Eclipse Purge-and-Trap Method Modifications:

Only the parameters which were modified are listed. All other set points are as listed in RSKSOP-122 Revision 4 page 6.

Optimized P&T conditions for C1-C4 Alcohols in water		
Parameter	Standard	Optimized
Trap type	#10	#7
Sample temperature	Ambient	60 °C
Purge time	6 minutes	11 minutes
Desorb preheat temperature	off	On at 180°C
Trap temperature during purge	Ambient	40 °C
Water management fitting temperature during desorb	Ambient	40 °C

Instrument Method:

The instrument method is the same as that listed in RSKSOP-122 Revision 4, as seen below. The calibration has been changed to contain only C1-C4 alcohols and their
isomers.

method: C:\CHEM32\2\METHODS\C1_C4 ALCOHOL.M\C1_C4 ALCOHOL.M
Modified on: 4/25/2012 at 9:49:13 AM

6890 GC METHOD

OVEN
- Initial temp: 35 'C (On)
- Initial time: 5.00 min
- Ramps:

#	Rate	Final temp	Final time
1	6.00	100	0.00
2	20.00	200	8.00
3	0.0(Off)		

- Post temp: 50 'C
- Post time: 0.00 min
- Run time: 28.83 min
- Maximum temp: 260 'C
- Equilibration time: 0.20 min

FRONT INLET (SPLIT/SPLITLESS)
- Mode: Split
- Initial temp: 50 'C (Off)
- Pressure: 0.00 psi (Off)
- Total flow: 45.0 mL/min
- Gas saver: Off
- Gas type: Helium

BACK INLET (SPLIT/SPLITLESS)
- Mode: Split
- Initial temp: 150 'C (On)
- Pressure: 6.74 psi (On)
- Split ratio: 0.1:1
- Split flow: 0.6 mL/min
- Total flow: 10.1 mL/min
- Gas saver: Off
- Gas type: Helium

COLUMN 1
- Capillary Column
- Model Number: J&W 125-1364
- DB-624
- Max temperature: 260 'C
- Nominal length: 60.0 m
- Nominal diameter: 530.00 um
- Nominal film thickness: 3.00 um
- Mode: constant pressure
- Pressure: 6.74 psi
- Nominal initial flow: 5.1 mL/min
- Average velocity: 33 cm/sec
- Inlet: Back Inlet
- Outlet: Front Detector
- Outlet pressure: ambient

COLUMN 2
- Capillary Column
- Model Number: J&W 1211114
- DB-624
- Max temperature: 260 'C
- Nominal length: 31.0 m
- Nominal diameter: 320.00 um
- Nominal film thickness: 1.80 um
- Mode: (see column 1)
- Pressure: 6.74 psi
- Nominal initial flow: 1.3 mL/min
- Average velocity: 23 cm/sec
- Inlet: Back Inlet
- Outlet: Back Detector
- Outlet pressure: ambient

FRONT DETECTOR (GC4450)
- Temperature: 250 'C (On)
- Hydrogen flow: 40.0 mL/min (On)
- Air flow: 375.0 mL/min (On)
- Mode: Constant makeup flow
- Makeup flow: 45.0 mL/min (On)
- Makeup Gas Type: Helium
- Flame: On
- Electrometer: On
- Lit offset: 2.0

BACK DETECTOR (PIDSIG)
- Electrometer: On

SIGNAL 1
- Data rate: 10 Hz

SIGNAL 2
- Data rate: 20 Hz

method: C:\CHEM32\2\METHODS\C1_C4 ALCOHOL.M\C1_C4 ALCOHOL.M
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Type: front detector
Save Data: On
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

Type: back detector
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

COLUMN COMP 1
Derive from front detector

COLUMN COMP 2
Derive from back detector

POST RUN
Post Time: 0.00 min

TIME TABLE

Time	Specifier	Parameter & Setpoint

GC Injector

Front Injector:
No parameters specified

Back Injector:
No parameters specified

method: C:\CHEM32\2\METHODS\C1_C4 ALCOHOL.M\C1_C4 ALCOHOL.M
Modified on: 4/25/2012 at 9:49:13 AM

Integration Events

Non signal specific Integration Events

Event	Value
Tangent Skim Mode	New Exponential
Tail Peak Skim Height Ratio	20.000
Front Peak Skim Height Ratio	20.000
Skim Valley Ratio	20.000
Baseline Correction	Advanced
Peak to Valley Ratio	500.000

Default Integration Event Table "Event"

Event	Value	Time
Initial Slope Sensitivity	1.000	Initial
Initial Peak Width	0.040	Initial
Initial Area Reject	1.000	Initial
Initial Height Reject	1.700	Initial
Initial Shoulders	OFF	Initial

Signal Specific Integration Event Table "Event_FID1A"

Event	Value	Time
Initial Slope Sensitivity	3.306	Initial
Initial Peak Width	0.103	Initial
Initial Area Reject	4.865	Initial
Initial Height Reject	0.395	Initial
Initial Shoulders	TAN	Initial

Apply Manual Integration Events: No

Calibration Table with Plots

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================================================================================
                              Calibration Table
================================================================================


Calib. Data Modified  :      4/24/2012 3:56:22 PM

Calculate             :      External Standard
Based on              :      Peak Area

Rel. Reference Window :      2.000 %
Abs. Reference Window :      0.000 min
Rel. Non-ref. Window  :      2.000 %
Abs. Non-ref. Window  :      0.000 min
Use Multiplier & Dilution Factor with ISTDs
Uncalibrated Peaks    :      not reported
Partial Calibration   :      Yes, identified peaks are recalibrated
Correct All Ret. Times:      No, only for identified peaks

Curve Type            :      Linear (some peaks differ, see below)
Origin                :      Included (some peaks differ, see below)
Weight                :      Equal (some peaks differ, see below)

Recalibration Settings:
Average Response      :      Floating Average New 0%
Average Retention Time:      Floating Average New 0%

Calibration Report Options :
    Printout of recalibrations within a sequence:
        Calibration Table after Recalibration
        Normal Report after Recalibration
    If the sequence is done with bracketing:
        Results of first cycle (ending previous bracket)

Signal 1: FID1 A,

RetTime   Lvl   Amount      Area     Amt/Area  Ref Grp Name
 [min] Sig      [ppb]
-------|--|--|----------|----------|----------|---|--|---------------
  6.399  1  1   50.00000    7.72840    6.46965        Methanol
            2  100.00000   14.37487    6.95659
            3  250.00000   33.48655    7.46568
            4  500.00000   65.95109    7.58138
            5 1000.00000  127.33865    7.85308
            6 2000.00000  253.71498    7.88286
  8.391  1  1   50.00000   60.17266 8.30942e-1        Ethanol
            2  100.00000  118.34559 8.44983e-1
            3  250.00000  305.34064 8.18758e-1
            4  500.00000  602.22833 8.30250e-1
            5 1000.00000 1192.22107 8.38771e-1
            6 2000.00000 2349.09814 8.51391e-1
  9.843  1  1   50.00000  173.56769 2.88072e-1        2-Propanol
            2  100.00000  328.54593 3.04371e-1
            3  250.00000  851.23224 2.93692e-1
            4  500.00000 1712.65564 2.91944e-1
            5 1000.00000 3338.23096 2.99560e-1
            6 2000.00000 6718.08301 2.97704e-1
 10.938  1  1   50.00000  436.51917 1.14543e-1        Tert Butyl Alcohol
            2  100.00000  845.62994 1.18255e-1

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RetTime [min]	Sig	Lvl	Amount [ppb]	Area	Amt/Area	Ref	Grp	Name
		3	250.00000	2181.03369	1.14625e-1			
		4	500.00000	4295.52930	1.16400e-1			
		5	1000.00000	8465.59375	1.18125e-1			
		6	2000.00000	1.69248e4	1.18170e-1			
12.677	1	1	50.00000	159.04778	3.14371e-1	+		n-propanol
		2	100.00000	301.40417	3.31780e-1			
		3	250.00000	786.15668	3.18003e-1			
		4	500.00000	1584.15601	3.15625e-1			
		5	1000.00000	3054.05835	3.27433e-1			
		6	2000.00000	6170.49902	3.24123e-1			
14.365	1	1	50.00000	317.38031	1.57540e-1			2-Butanol
		2	100.00000	608.55652	1.64323e-1			
		3	250.00000	1569.97827	1.59238e-1			
		4	500.00000	3145.65894	1.58949e-1			
		5	1000.00000	6179.34570	1.61829e-1			
		6	2000.00000	1.24065e4	1.61205e-1			
15.762	1	1	50.00000	391.51703	1.27708e-1			Isobutanol
		2	100.00000	751.86346	1.33003e-1			
		3	250.00000	1931.40845	1.29439e-1			
		4	500.00000	3878.64111	1.28911e-1			
		5	1000.00000	7664.20996	1.30477e-1			
		6	2000.00000	1.53577e4	1.30228e-1			
17.198	1	1	50.00000	253.30080	1.97394e-1			1-Butanol
		2	100.00000	475.53476	2.10290e-1			
		3	250.00000	1242.83899	2.01152e-1			
		4	500.00000	2474.64551	2.02049e-1			
		5	1000.00000	4787.57373	2.08874e-1			
		6	2000.00000	9630.36133	2.07677e-1			

More compound-specific settings:

Compound: Methanol
  Curve Type : Linear
  Origin : Included
  Calibration Level Weights:/
    Level 1 : 1
    Level 2 : 1
    Level 3 : 1
    Level 4 : 1
    Level 5 : 1
    Level 6 : 1

Compound: Ethanol
  Curve Type : Linear
  Origin : Included
  Calibration Level Weights:/
    Level 1 : 1
    Level 2 : 1
    Level 3 : 1
    Level 4 : 1
    Level 5 : 1
    Level 6 : 1

Compound: 2-Propanol
  Curve Type : Linear
  Origin : Included

Method C:\CHEM32\2\METHODS\C1_C4 ALCOHOL.M\C1_C4 ALCOHOL.M

Compound: Tert Butyl Alcohol
  Curve Type : Linear
  Origin : Included

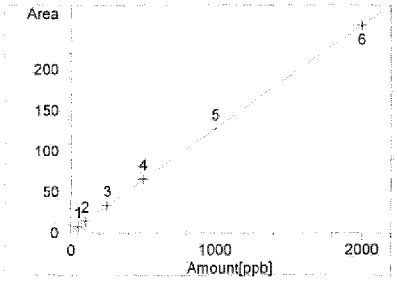
Compound: n-propanol
  Curve Type : Linear
  Origin : Included

Compound: 2-Butanol
  Curve Type : Linear
  Origin : Included
  Calibration Level Weights:/
    Level 1 : 1
    Level 2 : 1
    Level 3 : 1
    Level 4 : 1
    Level 5 : 1
    Level 6 : 1

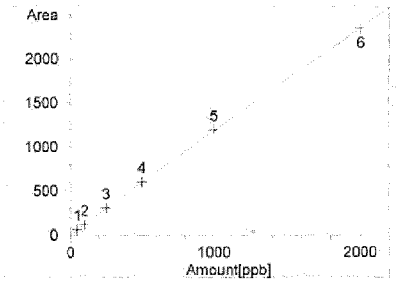
Compound: Isobutanol
  Curve Type : Linear
  Origin : Included

Compound: 1-Butanol
  Curve Type : Linear
  Origin : Included

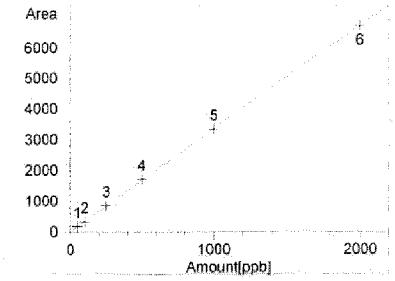
Calibration Curves



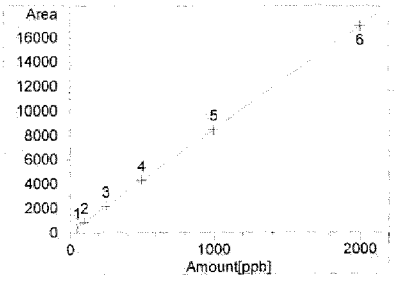
Methanol at exp. RT: 6.399
FID1 A,
Correlation: 0.99996
Residual Std. Dev.: 0.94833
Formula: y = mx + b
m: 1.26239e-1
b: 1.46617
x: Amount[ppb]
y: Area
Calibration Level Weights:
Level 1 : 1
Level 2 : 1
Level 3 : 1
Level 4 : 1
Level 5 : 1
Level 6 : 1



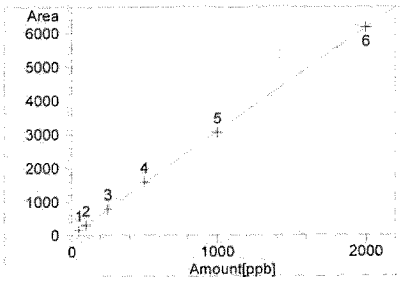
Ethanol at exp. RT: 8.391
FID1 A,
Correlation: 0.99996
Residual Std. Dev.: 8.52161
Formula: y = mx + b
m: 1.17526
b: 6.27105
x: Amount[ppb]
y: Area
Calibration Level Weights:
Level 1 : 1
Level 2 : 1
Level 3 : 1
Level 4 : 1
Level 5 : 1
Level 6 : 1



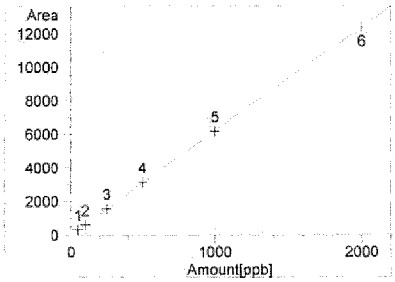
2-Propanol at exp. RT: 9.843
FID1 A,
Correlation: 0.99998
Residual Std. Dev.: 17.97541
Formula: y = mx + b
m: 3.35456
b: 5.64573
x: Amount[ppb]
y: Area



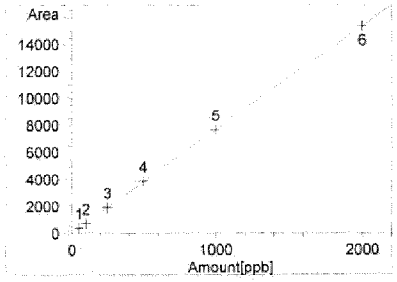
Tert Butyl Alcohol at exp. RT: 10.938
FID1 A,
Correlation: 0.99999
Residual Std. Dev.: 32.59024
Formula: y = mx + b
m: 8.45325
b: 25.92275
x: Amount[ppb]
y: Area



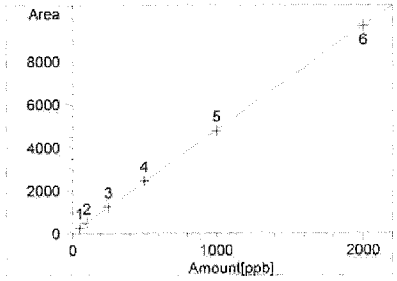
n-propanol at exp. RT: 12.677
FID1 A,
Correlation: 0.99995
Residual Std. Dev.: 23.62735
Formula: y = mx + b
m: 3.07893
b: 6.78454
x: Amount[ppb]
y: Area



2-Butanol at exp. RT: 14.365
FID1 A,
Correlation: 0.99999
Residual Std. Dev.: 23.67068
Formula: y = mx + b
m: 6.19779
b: 8.01113
x: Amount[ppb]
y: Area
Calibration Level Weights:
Level 1 : 1
Level 2 : 1
Level 3 : 1
Level 4 : 1
Level 5 : 1
Level 6 : 1



Isobutanol at exp. RT: 15.762
FID1 A,
Correlation: 0.99999
Residual Std. Dev.: 20.33585
Formula: y = mx + b
m: 7.67606
b: 5.53321
x: Amount[ppb]
y: Area



1-Butanol at exp. RT: 17.190
FID1 A,
Correlation: 0.99996
Residual Std. Dev.: 33.53921
Formula: y = mx + b
m: 4.80513
b: 17.74863
x: Amount[ppb]
y: Area

Sample Analysis:

The test samples were analyzed using the method outlined above. Several blanks were analyzed at the beginning of the sample queue followed by a Continuing Calibration Check standard (CCC) at 100 ppb and a Second Source Standard (SS) at 500 ppb.

The samples were analyzed sequentially following the Blank, CCC, and SS. The results of the analysis are summarized on table 1.

Table 1: Sample analysis results-analysis date 15-May-2012

8OA878DW BLACK= FIRST RUN WITH FULL 40 ML VOA units =ppb

SS 6359 RED=SECOND RUN WITH 5ML HEADSPACE USING SAME VOA VIALS AS FIRST RUN

SAMPLE	METHANOL	ETHANOL	2-PROPANOL	TERT BUTYL ALCOHOL	N-PROPANOL	2-BUTANOL	ISOBUTANOL	1-BUTANOL
PGDW20-0412	ND	ND	ND	ND	ND	ND	ND	ND
PGDW20-0412	ND	ND	ND	ND	ND	ND	ND	ND
EPAMW02-0412	592	28.4	51.7	5395	11.8	15.6	10.7	32.2
EPAMW02-0412	337	28.7	42.7	5448	10.6	10.4	10.9	29.6
PGDW30-0412	ND	ND	ND	ND	ND	ND	ND	ND
PGDW30-0412	ND	ND	ND	BQL-1.2	ND	ND	ND	ND
PGDW05-0412	ND	ND	ND	ND	ND	ND	ND	ND
PGDW05-0412	ND	ND	ND	ND	ND	ND	ND	ND
EPAMW01-0412	863	ND	ND	197	ND	ND	BQL-5.8	ND
EPAMW01-0412	894	ND	ND	54.4	ND	ND	BQL-2.1	ND
EPAMW01-0412D	831	ND	BQL-3.9	198	BQL-1.7	ND	BQL-5.5	BQL-1.9

EPAMW01-0412D	837	BQL-13.7	BQL-1.1	60	ND	ND	BQL-1.8	BQL-2.6
FIELDBLK4	ND	ND	ND	ND	ND	ND	ND	ND
FIELDBLK4	ND	ND	ND	ND	ND	ND	ND	ND

RESULTS AND DISCUSSION

The VOA vials containing the CCC and the SS were prepared as duplicates to those utilized in the ICAL (24-April-2012). The CCC was within 1% for all alcohols except methanol and ethanol with the ethanol value at -7% and the methanol at +200%. The SS was within 5% of the true value. The ending CCC was done at both 50ppb and 250ppb with recoveries in the 70-130% range. Subsequent reanalysis of freshly prepared CCC's demonstrated the validity of the calibration curve with recovery error less than 10% for all alcohols. This data demonstrates there are problems with refrigerated storage of prepared standards. In this case, the vials were stored at 4°C for about 3 weeks.

There are two sets of data in Table 1; the data in black is the first run of the VOA vials without any headspace. The second run of the vials (in red) was done the second day after the samples had set on the autosampler, at ambient temperature, overnight with 5 mls of headspace. There is one field duplicate in the sample set, ss#6359-5 and 6359-6. The RPD for the methanol value is 0.72% and the same value for TBA is 0.51%.

Literature Cited:

"Low-level Detection of Ethanol, 1,4-Dioxane, and Other Oxygenates Using the Eclipse Purge-and-Trap Sample Concentrator". OI Analytical Application Note 25370206 12 pages. March 2006.

RSKSOP-122/Revision 4. Analysis of Volatile Aromatic Hydrocarbons by Purge and Trap Gas Chromatography. John Cox. March 2007.

RSKSOP-248/Revision 1, Standard Operating Procedure Determination of Method Detection Limits. Steve Vandegrift, May 2004.

EPA method 8015C Revision 3. Nonhalogenated Organics by Gas Chromatography. February 2007.